AD-A193 569 HIERACHICAL STRUCTURE IN POLYMERIC SOLIDS AND ITS   1/1
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HIERARCHICAL STRUCTURE IN POLYMERIC SOLIDS AND ITS INFLUENCE ON PROPERTIES

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*2nd on work performed

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SUMMARY

Work was centred on the family of mesogenic polyethers (synthetized, Professor Percec, Cleveland, USA) which appear to be the model substance for liquid crystal polymers to date in aid of the exploration of polymeric structure hierarchy. Notable advance was achieved along two directions.

By embracing both lyotropic and thermotropic behaviour, coupled with crystallization from both states, and also from isotropic solution, the foundations were laid for a comprehensive investigation of generalized thermodynamic phase stability (phase diagram) and of the resulting morphologies with the ensuing structure hierarchy, to our knowledge for the first time in polymer science in its present completeness.

On the fine scale end of the hierarchy molecular and layer arrangements were studied in the various mesogenic and crystallizing phases, utilising X-ray diffraction from specially prepared oriented systems. In addition to a considerable amount of new information on the materials in question, the results bear directly on some general issues in polymer science, namely on ordering in random copolymers and on the nature of disorder in semi-crystalline lamellar systems.

INTRODUCTION

Research during the present period was exclusively concerned with the new polymeric liquid crystal model materials which have become available thanks to the cooperation of Professor V. Percec, Case Western Reserve University, Cleveland, USA. As laid out previously, by suitable choice of appropriate members of this family of compounds (see Fig. 1) all relevant states and corresponding transitions involving the liquid crystal phase (LC) could be attained and studied under practicable circumstances, including structure and morphology, with the aim of establishing a general scheme for structure hierarchy. During the present period the scope has widened considerably to an extent that thanks to Professor Percec's materials it is now likely to embrace the entire spectrum of states in polymeric matter, such as melt, solution, liquid crystal(LC) both thermotropic and lyotropic, and the crystalline state possibly including previously unrecognized variants. In addition, and unexpectedly, the new materials promise to be models also for the general issue of copolymer-homopolymer behaviour and promise to provide new levers to the much debated fundamental and practical issue of the nature and location of disorder (amorphous component) within semi-crystalline polymers in general with correspondingly important implications for structure hierarchy. In view of the above widening horizons, other aspects of the original program (flow orientation) relying on less tractable model material (PBT) have been kept in abeyance. This is in the expectation that once the background to Professor Percec's new materials has been worked up there will be an easier and more productive passage towards that goal.

To recapitulate, the materials are polyethers constituted of stylbene and alkane members as shown in Fig. 1 where n (the number of alkane units) is variable from one component to another (homopolymers) and can be of more than one kind even in the same chain (copolymers). (for nomenclature see caption of Fig. 1).

The work was along two lines: I. Phase transitions - morphology, II. Molecular features by X-ray diffractions. Currently I and II are still along somewhat separate lines, but it is anticipated that they will merge in the quest of comprehensive knowledge.

I PHASE TRANSITIONS - MORPHOLOGY

General - New Scope

The most far reaching recognition of the work during the present period was the fact that the newly available polyethylers can, in addition to being thermotropic, also be lyotropic. This offers the opportunity to explore the full phase diagrams of a liquid crystal forming substance embracing all concentrations up to the pure melt (thermotropic) also including crystallization, and all this combined with the wide ranging structure-hierarchies arising. To our knowledge it is the first time that this is possible, widening immeasurably the scope of this branch of science.

The experimental basis is provided by the fact that the new polymers are soluble in certain commonly available solvents in all proportions enabling all lyotropic states up to the thermotropic to be

realized, where on subsequent cooling crystallization from either of these states can then be achieved. This could not be realized previously in a purposeful and comprehensive manner.

Thanks to the work during this period and to the recognition that ensued, the full phase diagram of a polymer, which can form both liquid crystal and true crystals, and which is both soluble and fuseable can now be formulated as in Fig. 2. This phase diagram, while directly following from thermodynamics, has never been formulated in its completeness before. To facilitate appreciation the ingredients constituting it will now be presented. These ingredients, which on their own, have formed the basis of all past studies on polymer phase transitions but are being here compounded for the first time, are as follows:

Fig. 3. General,isotropic liquid$\rightarrow$liquid phase separation
Common situation for solvent-polymer and polymer-polymer systems.

Fig. 4. The same as in Fig. 2, except that one component, the polymer, is liquid crystal forming. This is the subject established and developed by Flory, who predicted the existence of a biphasic region, (with the vertical "chimney") for LC forming rigid rod polymers.

Fig. 5. Crystallization from solution with mutually immiscible solid components. This is the situation in the usual studies of polymer crystallization from solution.

With some loss of generality by confining ourselves to polymer-low molecular wt. solvent systems, where the latter neither crystallizes nor forms liquid crystals, (the general situation, without these restrictions is even more interesting, but would be difficult to present, here in brief) the combination of phase equilibria underlying Figs 3-5 yields Fig. 2. The meaning of the different lines and zones are explained in the caption. The T_g (glass transition), although not a thermodynamic feature, is significant, as through it the onset of vitrification will arrest any phase transition which would occur otherwise. For concentrations intermediate between c=0 and c=1 it will lie in between T_g^s (solvent) and T_g^p (pure polymer), more exactly, depending on the system under consideration, and of course will only apply to the amorphous component of a semicrystalline or supercooled system.

The region denoted as biphasic represent collectively all mesophases. There should be further subdivision within it (not represented here) defining the stability regions of the different types of mesophase such as nematic, smectic etc.

The above (still simplified) scheme is the canvas on which the future science of crystalline and liquid crystalline (LC) polymers in the presence and absence of solvent (or with any further polymer components) will need to be depicted, and ourselves have the materials and facilities to do so.

Phase stability as in Fig. 2 define the stability criteria of the various phases, but in itself say as yet nothing about the morphologies which need to be assessed separately. The latter was one of the main items of our original programme. This will now be pursued with widened prospects in combination with the exploration of the newly arisen

thermodynamic stability conditions, i.e. the phase diagram. The phase diagram is a necessary but not sufficient condition for identifying microstructure and structure hierarchy.

The actual experimental work which has led to the above recognitions has so far been confined to the extremes of the concentration ranges:
a)   Thermotropic polymer (c=1.0 in Fig. 2)
b)   Dilute solutions (c=0.2%)
We believe significant advances were made along a) even if on conventional lines. It was the work under b) which has opened up the new horizons.

A. Thermotropic state (c=1 in Fig. 2)

As stated in previous report the newly available polyethers have the unique advantage over most other currently studied thermotropic LC polymers that with them the full range of transitions, isotropic $\rightleftharpoons$ LC (T_i) and LC$\rightleftharpoons$true crystal (T_m),together with the intervening glass transition (T_g) can be explored. For some of the polymers this was mapped previously (Fig. 4 of report March 1986). In current DSC experiments this was pursued primarily with the aim of assessing the effect of sample treatment conditions on these transitions and the associated heat effects as a preliminary to morphological investigations.

The principal outcome of this still ongoing work is as follows:

i)   All heat effects are a function of original sample preparation and posttreatment conditions. This is illustrated for the case of PHMS- 5-7 in Fig. 6, where the post annealing conditions were varied systematically. It follows, that on its own just any arbitrary chosen sample provides inadequate information, and can in fact be misleading for the thermodynamic characterisation of the processes involved.

ii)   By utilising the change in heat capacity ΔC_p at T_g, and by relying on the relation

$$\Delta C_p / \Delta C_p{}^O = 1 - W_c$$

where $\Delta C_p{}^O$ refers to the fully amorphous sample and W_c is the crystal weight fraction, a linear relation between ΔH (the heat of fusion) and ΔC_p could be established

$$(\Delta H = \Delta H^O - (\Delta H^O / \Delta C_p{}^O) \cdot \Delta C_p$$

with ΔH^O (the heat of fusion of crystal) – see Fig. 7. This enabled the establishment of ΔH^O by extrapolation giving $\Delta H^O = 337/g$. Similarly, from $\Delta H^O / \Delta S^O = T_m$ we get the entropy of fusion, ΔS^O, which turns out to be 0.089 J/q.K. The latter provides a measure of the change in degree of order on going from crystalline to the LC (here nematic) state. It follows from the above value for ΔS^O that this change is small when compared with conventional flexible polymers.

iii)   The procedure used under i) and ii) was carried over to the homopolymer PHMS- 5 and was found to be applicable. ΔH^O and ΔS^O values were found to be identical to those for the copolymer within the error of extrapolation. This leads to the important conclusion that there is

no significant difference in thermodynamic stability between crystal in the homo and copolymer, the main difference being in the achievable maximum degree of crystallinity (lower in the copolymer, 35%, as opposed to 85% in homopolymers). This means that only the amount of crystal will be affected but not the perfection by the copolymer content.

iv) The enthalpy and entropy associated with the LC$\rightarrow$ isotropic transition are smaller, about ^{1}/5, than those found for the crystal $\rightarrow$LC transition. It follows that the LC state is closer to the melt than to the crystal as regards ordering, we believe a significant finding.

A) Lyotropic state - solution crystallization

Having become aware of the fact that our materials are readily soluble, solution studies were undertaken. In the first instance this was to see how the present polyethers consisting of mesogenic groups linked with flexible spacers crystallize from solution, and in particular, whether they give rise to chain folded lamellar crystals such as are the basic structural entities in conventional crystalline polymers. It was in the course of this enquiry that an unsuspected wealth of new effects emerged which has led to the recognition that a phase diagram of the kind as in Fig. 2 must be operational linking solution with melt behaviour in a continuous fashion.

The investigations so far were confined to the homopolymer PHMS - 5, high molecular weight. Most of it was with xylene, some with chlorobenzene as solvent. Rather arbitrarily 0.2% was chosen, believed to be representative of dilute solutions. When in the case of xylene, the isotropic solution was cooled a range of effects were observed which made us realize that we must be moving along a path corresponding to the arrowed vertical dashed line in Fig. 2. (Or rather the sequence of effects observed suggested the existence of the kind of phase diagram as in Fig. 2). Further, another sequence of effects was observed as the solutions were drying in, indicating the moving horizontally in the direction of increasing c (concentration) towards c=1 (i.e. solvent free, thermotropic state) at some temperature corresponding to the horizontal arrowed dashed line in Fig. 2. The experimental material consists of numerous well documented photographs of which a few examples will be lifted out here.

Fig. 8 represents the first features seen as a solution is cooled from a temperature T_A. The higher birefringent still fluid spherical drops leave little doubt of their representing a lyotropic mesophase, hence that we are in the biphasic regime (dotted) of Fig. 2. The birefringent spheres would then represent the polymer-rich phase (which is LC in this case of a mesogenic polymer) and would correspond to the right side end point (y) of a horizontal tie line in Fig. 2. The isotropic solvent-rich phase (the dark featureless background in Fig. 8) would then correspond to the left end of the same tie line (q in Fig. 2).

On further cooling, each of the above phases will cross the crystal stability boundary (heaviest line in Fig. 2). Here the concentrated phase (LC droplet corresponding to point y, moving downwards along the coexistence boundary to point z) becomes structured (Fig. 9) as the polymer crystallizes within it (a LC$\rightarrow$crystal transformation with solvent ejection). This transformation was very characteristic.

In contrast, crystals of a large variety were appearing from what we hold to be the solvent-rich (i.e. polymer-poor phase). In the phase diagram this corresponds to a downward movement of point q to x, and beyond, along the heavy line to point B. The appearance of these latter crystals is expected to be the analogue of conventional polymer crystallization. The multitudinous forms this takes in the present case is undoubtedly due to the fact that during the present initial experiments the solutions were becoming more concentrated. I.E. material still in solution within the isotropic phase at point B crystallizes in a range of morphologies as the concentration increases from c_B to $c=1$. Some of the features we attribute to crystallization from the polymer-poor phase in fact became only visible after drying of the solution (i.e. at $c=1$). Even if conditions of formation are still ill defined in our present experiments, the resulting structures seem definite, with the variety probably corresponding to the different concentrations at which they formed. Fig. 10 shows one class of structure: birefringent rodlets with identifiable (on close inspection) periodic cross bandings (in the company of the brightly birefringent globular structures which are the aforementioned crystallization products from the polymer rich phase). Fig. 11 shows another class observed in the fully dried state: birefringent platelets. The birefringence here was uniform and could be extinguished by rotating the sample with relation to the polaroids.

Preliminary attempts were made to identify and further pursue all the above morphological features under the electron microscope. These are necessarily restricted to those obtainable in the dried state. Most of the entities were too thick for direct transmission and will call for more elaborate sample preparation methods in the future. Even so some noteworthy information was obtained. Some of the crystalline globules, while opaque for the beam, displayed angular outlines suggesting crystallographic habit (fig. 12) in line with some bright-field optical observations which indicated an underlying lamellar morphology. The electron-microscopic identification of the rodlets (Fig. 10) is still outstanding, nevertheless thin bladelike features were observed (Fig. 13) which could either be incipient rodlets or new features altogether. The EM equivalents of the platelets (Fig. 11) have not yet been found, nevertheless ubiquitous electron diffraction patterns, as in Fig. 13a, were observed. By all past precedent in conventional polymer crystals, these should correspond to lamellar crystals with chains perpendicular to the basal planes, hence to chain folding. The identification of the correponding morphological entity in the real space image is still outstanding. Even so, on the basis of the diffraction pattern a two-chain orthorhombic unit cell, reminiscent of highly ordered smectic E in low molecular weight LC-s, could be provisionally postulated.

In conclusion, while the morphological information is undoubtedly sketchy at present, it reveals a previously unsuspected wealth of new features. This, particularly and chiefly, in relation with the newly recognized phase stability criteria, opens up new dimensions for the study and utilisation of polymeric phase equilibria, phase transformations, microstructure, and through it all, for the full appreciation of structure hierarchy.

II. MOLECULAR STRUCTURE - LAYER PACKING

In this part of the programme we are examining the molecular ordering and entities arising therefrom by X-ray diffraction. In contrast to the microscopic morphology this is at the fine scale end of the structure hierarchy.

General Issues

1) As apparent from the chemical formula (Fig. 1) the mesogenic unit itself is asymmetric in the sense that the left-right (or up-down if held vertically, directions (as indicated by the arrow) are non-equivalent. This implies a source of orientational disorder in crystalline mesogenic layers (appropriate mixture of up-down sequences) which we believe may well be instrumental in mesophase formation.

2) The mesogenic units and flexible aliphatic spacers have widely different cross sectional areas with the consequences that, even if they are all identical (homopolymer case), both cannot pack equally closely laterally when in lateral register, forming layers (Fig. 14). Thus, if the mesogenic units with larger lateral cross sections pack closely (crystallographically) packing in the spacer layer will be loose, hence these layers will be sources of disorder. This has a close analogy with the crystalline-amorphous layer sequence in the common flexible polymers, (say polyethylene), hence bears on the issue of order-disorder sequence in polymeric materials in general.

3) When the *flexible spacers* are not equal and in random sequence, the question arises as to what determines the layer periodicity, or alternately, how are these spacers accommodated by a layer lattice as in Fig. 14?

The issue under 1) is currently only a realization (arisen during the work) which, nevertheless, is likely to be of potential consequence for designing mesophase forming materials and for evaluating and utilising their structure.

Issues 2) and 3) feature, even at the present early stage, directly in the interpretation of the current X-ray diffraction work to be presented below.

X-ray Diffraction

Experimental

In line with the first works reported in the previous report the samples were obtained in an oriented form. This has three fold significance: a) for the potential fibre forming ability of these materials, b) for flow induced orientation (and subsequent relaxation) of mesogenic materials, an objective on its own, c) for obtaining X-ray diffraction patterns with maximum information content. While a) and b) are also within our wider scope, it is c) which has been the more explicit objective of the work during the present period.

The fibres were drawn while in the nematic melt (utilising knowledge gained from the phase diagram (Fig. 2)) and quenched to room temperaure so as to preserve orientation (for which knowledge of T_g was

necessary - Fig. 2 and Fig. 4 (of previous report)). The oriented samples were subjected to various heat treatments and were examined by X-ray diffraction in situ at appropriate temperatures between T_m and room temperature.

Results and Interpretation

The X-ray diffraction patterns, Figs 17-22 should serve as representative examples of the numerous patterns which were obtained throughout the work, and support the conclusions which, not being presentable analytically in brief, will merely be quoted.

The information content of these patterns is of two kinds:
i) equatorial reflections and/or halos, i.e. centred on the horizontal bisector of the patterns. These provide information on interchain packing, which is essentially that of the mesogenic groups, ii) meridional reflections (i.e. lying along the vertical fibre direction). These define the crystallographic repeat period along the overall chain direction, and where appropriate, the layer periodicity.

Five different crystal types(A,B,C,D,T) were established each with a message of its own.

Form A. (Figs 17 and 18) obtained on PHMS-5. the structure here is with layers perpendicular to chains as in Fig. 14 (layer periodicity, L, measured: 20.5A, calculated: 20.0A). In the quenched sample (fig. 17) the equatorial reflections are broad and diffuse corresponding to a glassy nematic structure. In the annealed sample (Fig. 18) the equatorial reflections are sharp indicating crystalline packing. The reflections can be indexed on an orthorhombic unit cell with a = 7.7A, b = 7.3A, c = 20.5A. This struucture corresponds possibly to monotropic (supercooled) smectic E.

Form B. (Fig. 19) obtained on annealing PHMS-5 at 115°C. Note that meridional periodicity is 10.4A, i.e. half that for strucuture A. this suggests an interdigitating structure as in Fig. 15. This structure would relieve the large density deficiency arising in the layer formed by the spacers in fig. 14, but at the expense of the layer formation due to the mesogenic groups, which normally is the natural trend for such groups. Thus, contrasting A and B reveals a basic trend, that of a competition between achieving densest overall packing (B) and layer formation of the mesogens(A). Structure B is particularly favourable for PHMS-5 where length of mesogen and spacer are closely similar, hence this polymer is well suited to demonstrate this trend.

Form C. (Fig. 20) Obtained from PHMS-5 when pattern was recorded at 132°C, and from copolymer PHMS-5,7(50/50) under most circumstances. Here, the meridional reflection is split about the fibre axis through 18°.This, together with the doubling of the fibre periodicity (38A, apparent from off-equatorial reflections) suggests a tilted layer structure with inclination ∿18°) with a two mesogen unit cell along c (Fig. 16). Note that inclination of the layer interface is one way to reduce the packing deficiency in the spacer layer, a principle well appreciated in the field of lamellar structures with non-matching interfaces.

10

Form D (Fig. 21). Observed with PHMS-9. Here the layer interface is perpendicular to the fibre axis, however, the long period (L) has increased only little (2A) beyond that in PHMS-5; by the chemical formula an increase of 5A would be expected for identical structure. This is likely to mean that the spacer molecule is far from its extended form, hence is disordered. The latter would be the consequence of the large density deficiency which would arise otherwise.

Form T (Fig. 22). Unstable for PHMS-9 but the stable form of PHMS-9,11 (20/80) copolymer characterized by very large layer obliquity (∿40°). This can be taken as a manifestation of the general trend that the more tilted interfaces are the preferred ones for longer spacers as means to reduce packing deficiency, which these longer spacer chains can realize more effectively.

There are many further details, particularly relating to Forms D and T, which will not all be listed beyond stating that they support the general trends enunciated. Regarding a general principle relating to the copolymers, the conclusion in the previous report has gained further support: namely, that the overal layer periodicity conforms more closely to that due to the shorter spacer comonomer than to the longer one or to the mean of the two. We now see, that this arises because of the density deficiency in the spacer layer. Namely, if the thickness of the spacer layer is determined by the extended form of the shorter comonomer, the excess length of the longer one can be accommodated if the latter takes up a more contracted, hence disordered form. It also follows that, unless the situation in form B arises (Fig. 15), the crystalline packing within the mesogen will be unaffected by the copolymer nature of the chain. The latter was exactly the conclusion arising from the DSC measurements yielding H° and S° as described earlier in this report.

As a final generalisation: the present structures, in addition to being models for LC polymers, also prove to be models for the coexistence of ordered and disordered layers for polymer structures in general.

Figure Captions

Fig. 1   Constitution and chemical formula of our family of liquid crystal forming model polymer
Nomenclature: PHMS stands for polyhydroxy-α-methyl stilbene (mesogenic group). The numbers 5,7 and 9, 11 denote the number of carbon atoms constituting the flexible spacer. Single number denotes homopolymer, the numbers like the pair of 5,7 or 9, 11, a random copolymer constituted by such units in proportions as additionally specified (e.g. 50/50 or 20/80).

Fig. 2   Expected phase diagram of a liquid crystal (LC) and true crystal forming (Cr) polymer which is both fusable and soluble in a low molecular weight solvent in all proportions. Notations: Iso ≡ isotropic solution and melt; LC ≡ liquid crystal; Cr ≡ true crystal (polymer); Cr^S ≡ crystal of solvent; T_i ≡ isotropization temperature (liquid crystal melting) in the thermotropic state; T_m ≡ crystal melting temperature in the thermotropic state

T_g ≡ glass transition of pure (amorphous)polymer

T_g^S ≡ glass transition of solvent, E ≡ crystal eutactic point

for polymer-solvent pair.
Some guide lines for reading diagram; Dotted region, including bent "chimney" is the biphasic region where Iso and LC phases coexist with compositions corresponding to the end points of the appropriate horizontal (i.e. "tie") lines such as q and y. The heaviest line defines the upper stability of the polymer crystal (and below E that of solvent crystal) as a function of concentration (note there is a gap between points x and z). The narrow triangular region along the right hand side corresponds to polymer crystals with equilibrium amount of solvent; in practice this region is so narrow that it is usually ignored. The vertical dashed line with arrows (starting from T_A) is the type of cooling pathway followed in our experiment (here displaced to a much higher concentration for presentational purposes). The horizontal dashed line with arrows, starting from point B (concentration c_B) denotes the pathway of increasing concentration (drying in) in our experiment.

Figs 3,4,5 are the constituents from which Fig. 2 is constructed.
Fig. 3.   Liquid-liquid coexistence boundary.
Fig. 4.   Liquid-liquid coexistence curve where one component is a lyotropic liquid crystal.
Fig. 5.   Conventional phase boundary of a flexible (non liquid crystal forming) polymer and solution.

Fig. 6.   DSC thermograms of PHMS-5-7
Copolymer (M_w = 12,800) annealed at 77°C for different lengths of time (t_A)
a) quenched; b) t_A = 10 min; c) t_A = 20 min
d) t_A = 40 min; e) t_A = 60 min.

Fig. 7. ΔH v. ΔC_p as derived from the thermograms of Fig. 6 yielding ΔH^o when extrapolated to $\Delta C_p = 0$.

Fig. 8. PHMS-5 (homopolymer) in xylene
Liquid crystal droplets in an isotropic solution phase.
Photomicrograph, Crossed polaroids ~ 100X.

Fig. 9. Solidified (crystalline) droplets of Fig. 8 (above) on cooling to room temperature (particulars as Fig. 8).

Fig. 10. Banded rods forming in evaporating isotropic solution of PHMS-5 in xylene, in the presence of crystallized globules (particulars as in Fig. 8).

Fig. 11. Uniformly birefringent platelets of PHMS-5 after drying of solution (particulars as in Fig. 8).

Fig. 12. Transmission electron micrograph of PHMS-5 globules (as in Fig. 9).

Fig. 13. Transmission electron micrograph of entities (incipient or thin rods ?) grown on EM grid.

Fig. 13a. Electron diffraction pattern from a carbon support film on which a solution of PHMS-5 had been evaporated.

Figs 14-16. Structure schemes of PHMS polymers as arrived at from X-ray diffraction patterns from oriented fibres.
Fig. 14. Form A, perpendicular layer structure.
Fig. 15. Form B, staggered structure.
Fig. 16. Form C, inclined layer structure.(Fibre axis ∠ layer normal)

Figs 17-22. X-ray diffraction patterns from fibres of PHMS polymer. Fibre axis vertical.
Fig. 17. Nematic glassy structure (Form A)in polymer PHMS-5
Fig. 18. More crystalline version of Form A in polymer PHMS-5
Fig. 19. Form B in polymer PHMS-5
Fig. 20. Form C in polymer PHMS-5
Fig. 21. Form D in polymer PHMS-9
Fig. 22. Form T in copolymer PHMS-9-11.

RESEARCH PLANS

The progress during the present period sets clear indicators for the near future. The possibilities are virtually limitless. The phase diagram in Fig. 2 needs first explicit documenting; it will be the first time in polymer science that the possibilities inherent in this diagram will be systematically explored. This will provide the phase stability criteria. Concurrently also the morphology of the different solid phases will be followed up with particular emphasis on structure hierarchy. This will be the first instance that the lyotropic and thermotropic states will be linked in a combined thermodynamic and morphological study and also the first instance of following crystallization from the liquid crystal state from either category of liquid crystal. The effect of changing chemical constitution gives a further dimension to it all, which will be possible thanks to cooperation offered by Professor Percec, Cleveland. We have explicit expectations from increasing the flexible spacer length even in the homopolymer from the theoretical work by Papkov the 'chimney' in Fig. 2 should widen; Advances in Polymer Science v.59,1985) which amongst much else we are in a unique position to follow up.

The inherent potential of exploring molecular and layer packing offered by current X-ray diffraction will be followed up as a function of spacer length and physical treatment. In particular, correlation between thermodynamically identified state of matter and X-ray information will be pursued. Special emphasis will be given to the subdivisions within the liquid crystal phase (nematic, various smectics etc.) and to the relation between homo and copolymers. This line of the work should throw light on the fine scale end of the structure hierarchy. In fact, we shall attempt to penetrate to the molecular level itself by conformational analysis based on the current X-ray results.

The study of melt orientation, originally proposed is being deferred in view of the other promising opportunities arising with Professor Percec's new materials. It is being hoped to return to it later using these new materials once their basic behaviour has been mapped and once they are available in large quantities. We consider this more promising than to struggle with the much less tractable conventionally available thermotropics. In fact such orientation work is already in progress implicitly when preparing fibres for the X-ray studies. Examination of the effect of all the structural features on properties will follow at a later stage.

ADMINISTRATIVE ACTIONS

Dr. A.J. Owen left employment on the grant 31st August for personal reasons of his own. We replaced him with J.L. Feijoo (Simon Bolivar University, Caracas, Venezuela) as from 1st September 1986).

MAIN CHAIN LIQUID CRYSTAL FORMING COPOLYMERS WITH ETHER LINKAGE

PHMS-5-7 synthesised by V. Percec and-9-11
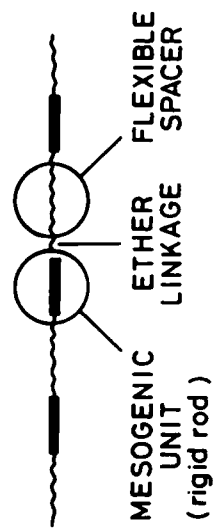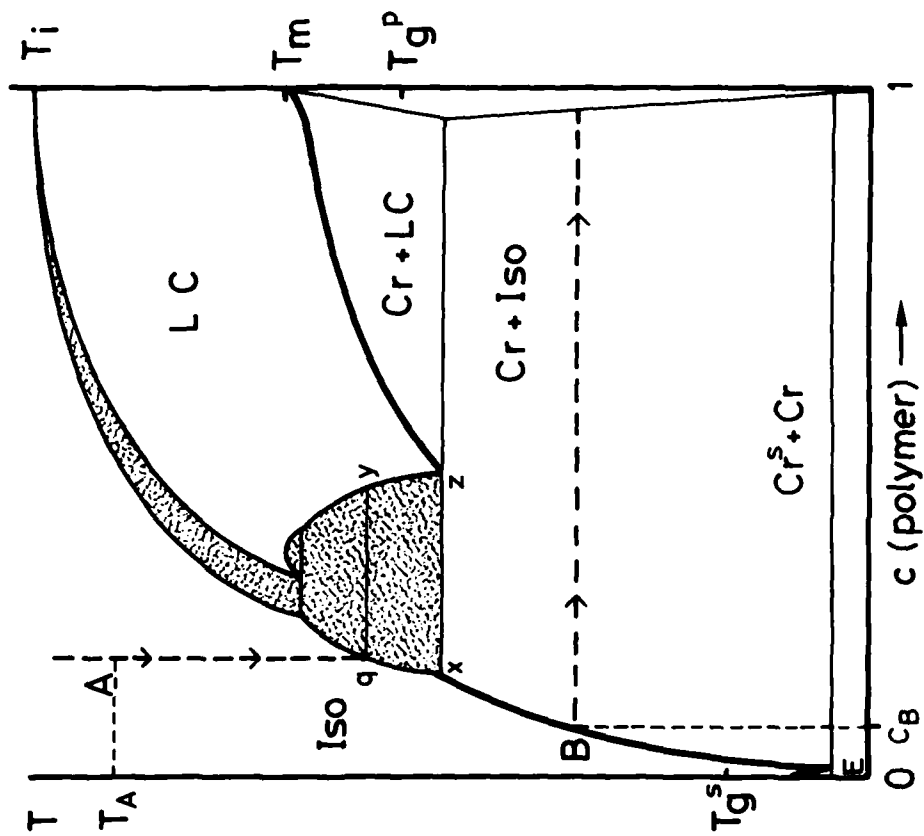
Linear macromolecule

MESOGENIC UNIT (rigid rod)

ETHER LINKAGE

FLEXIBLE SPACER
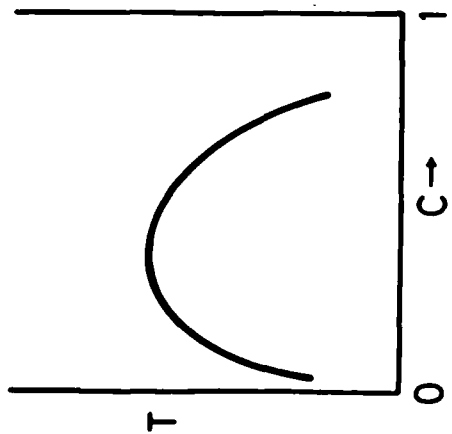
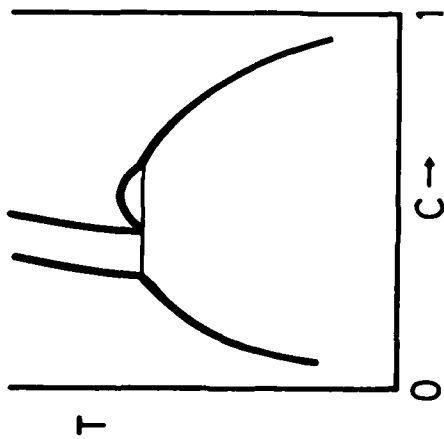$\{CH_2\}_n$
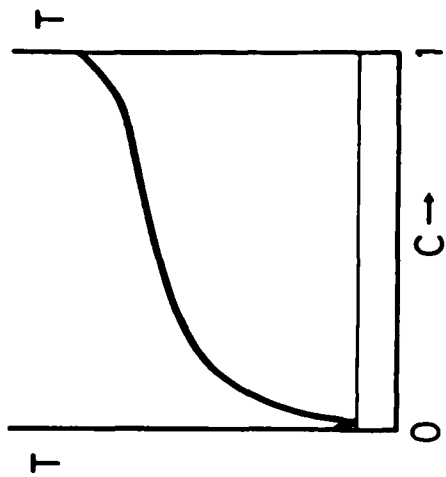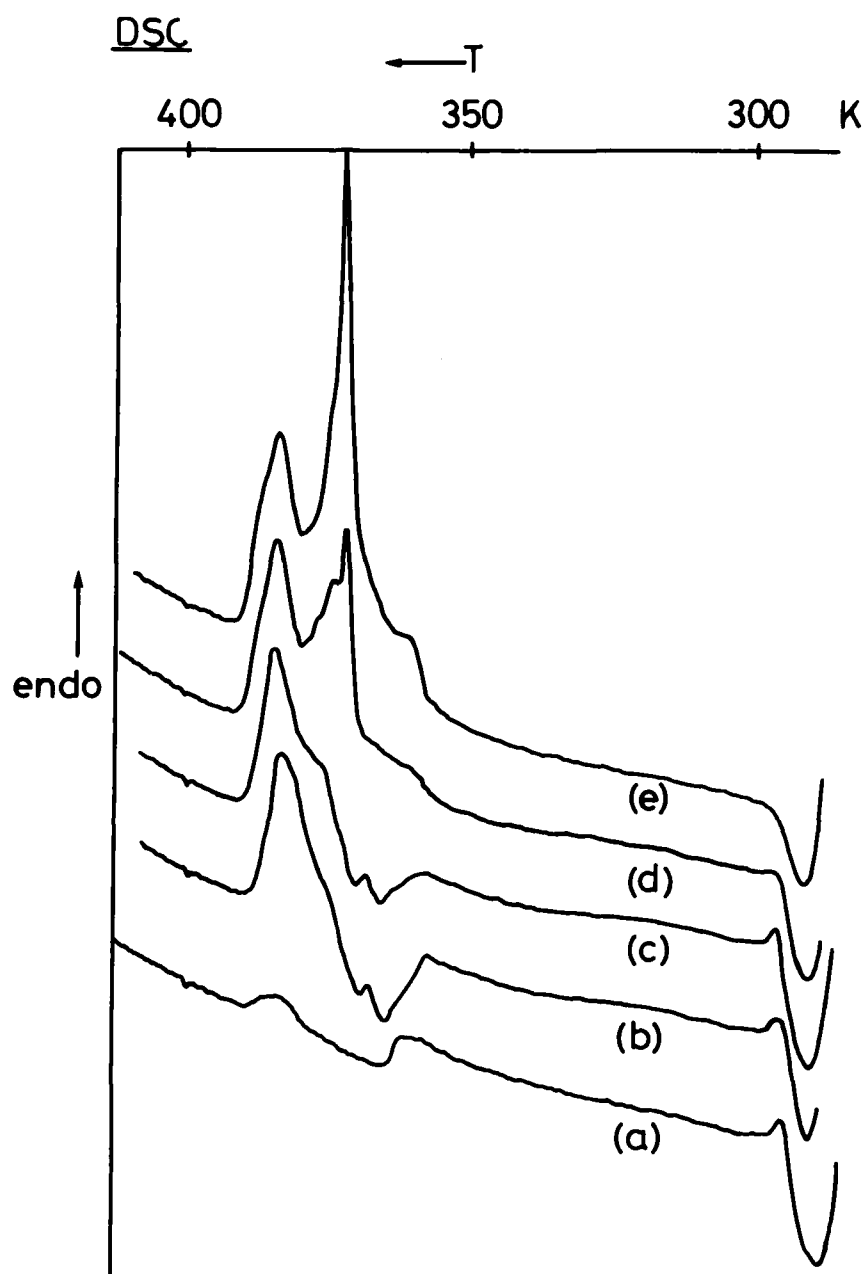n = 5 or 7
or n = 9 or 11
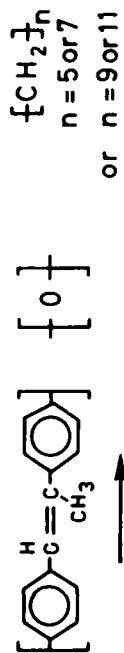
Fig. 1

Fig. 2

Fig.3

Fig.4

Fig.5

PHMS-5-7 (Mn = 12,800.)
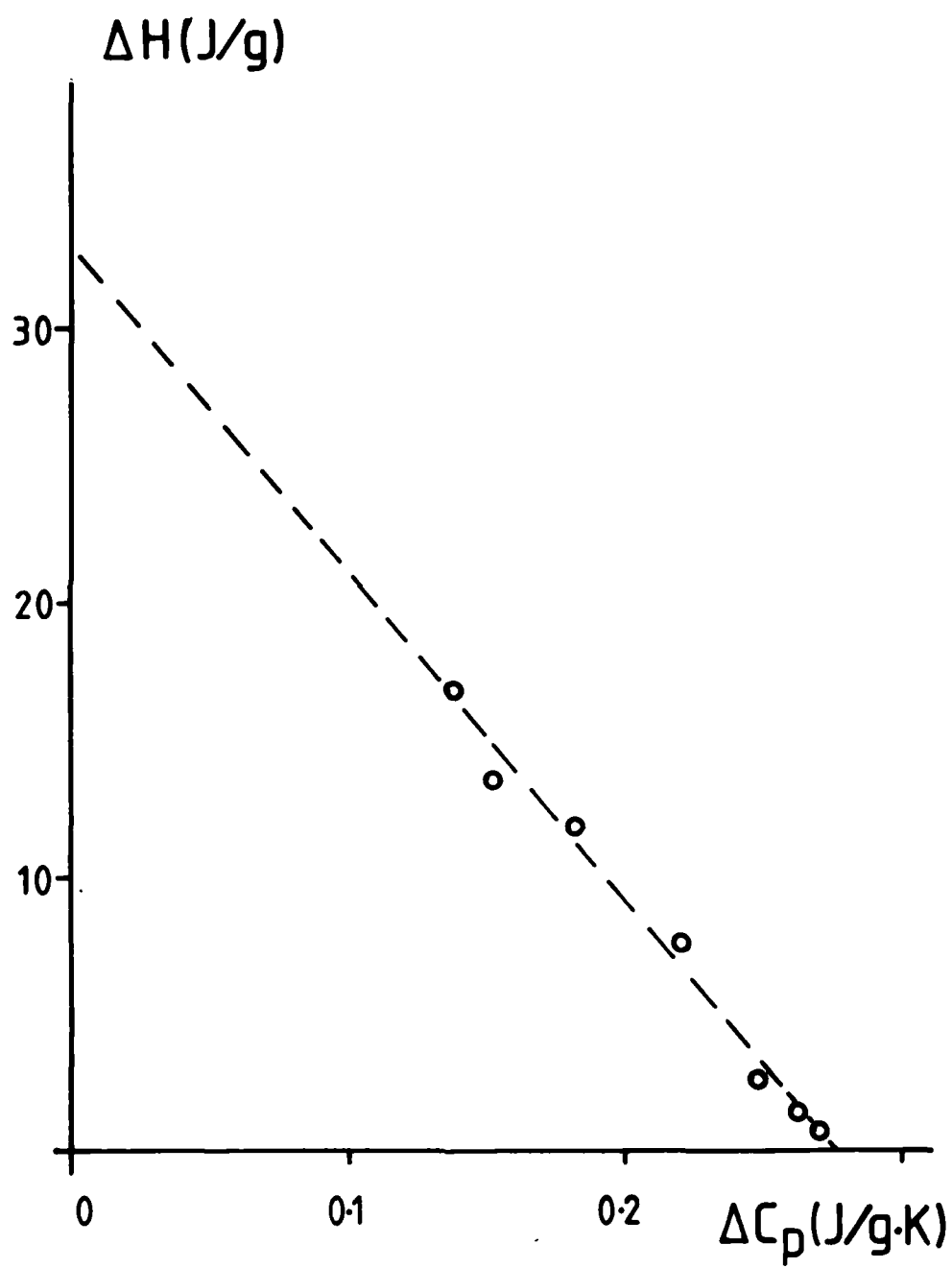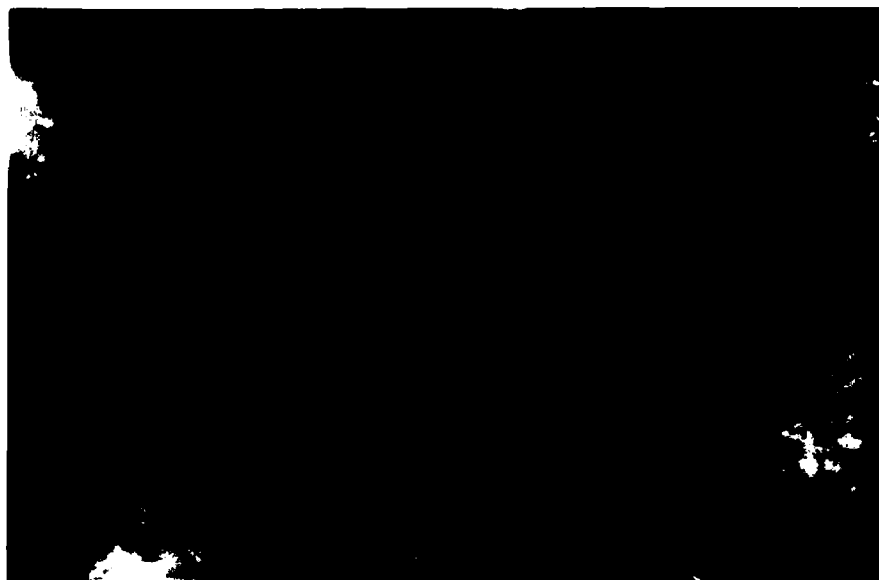Annealed at 350 K for times of
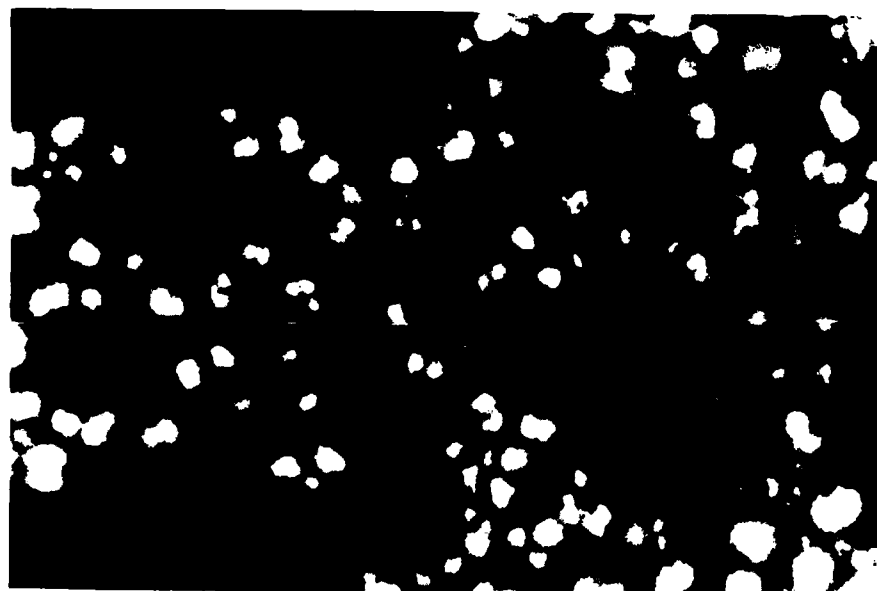a) quenched b)10 mins c) 20 mins d) 40 mins e) 1 hr
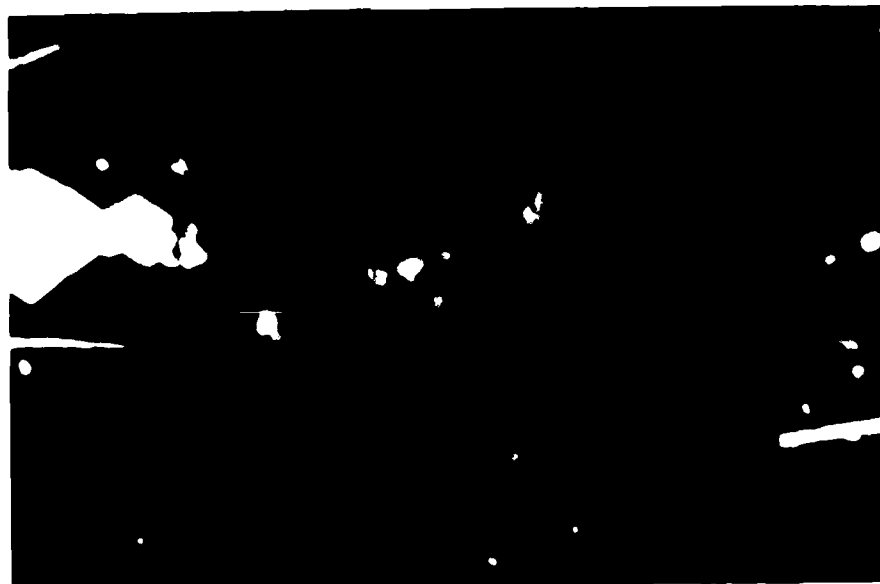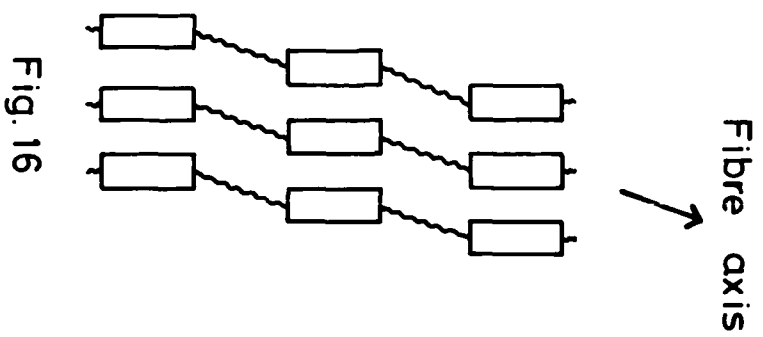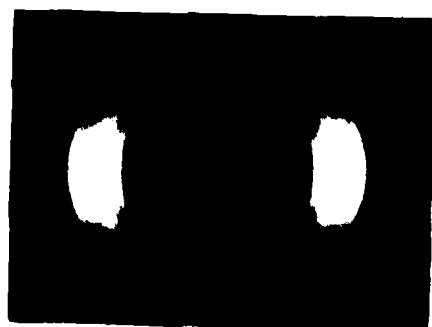
Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig.11
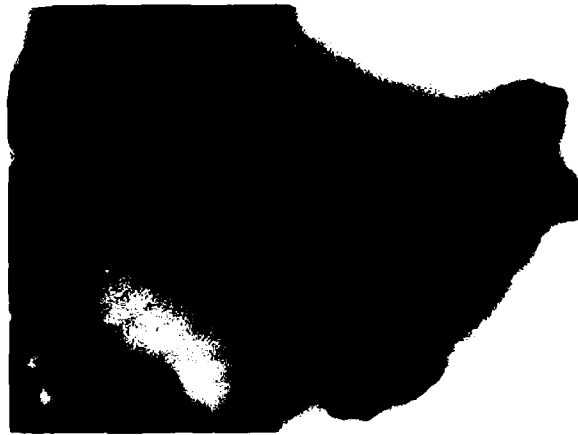
Fig.12

Fig.13

Fig. 13a

Fig. 14

spacer

mesogen

Fig. 15

Fibre axis

Fig. 16

Fibre axis
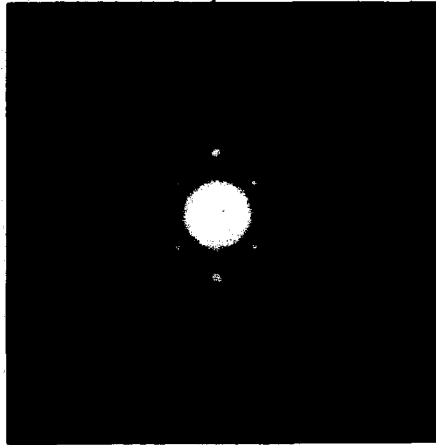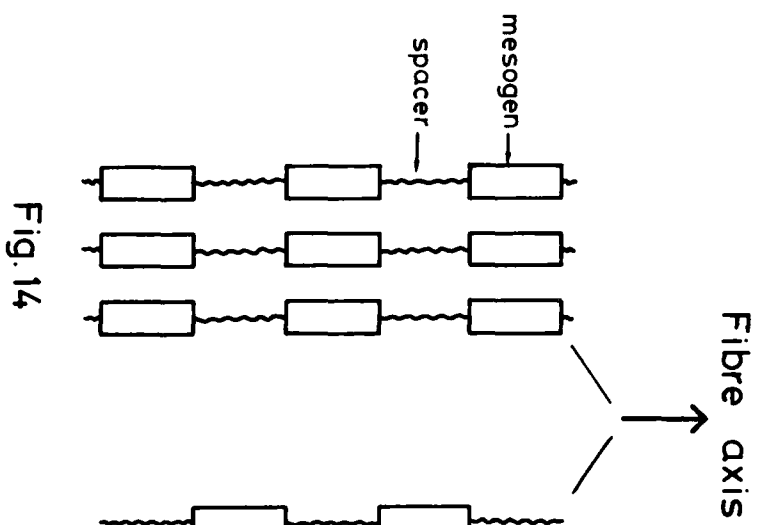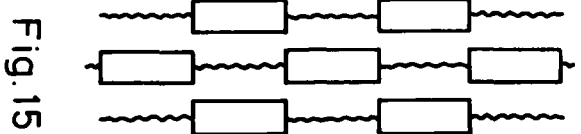
Fig. 17
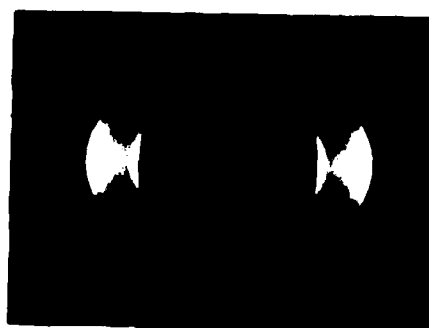
Fig. 18

Fig. 19
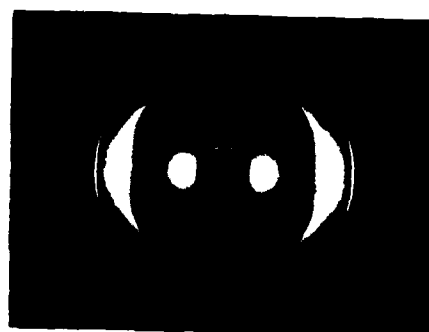
Fig. 20
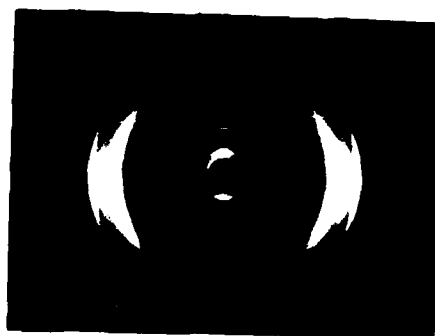
Fig. 21

Fig. 22

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